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Phase Equilibria in the $AgGaS_2$–GeS_2 Systems

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The $AgGaS_2$–GeS_2 section has been investigated using the methods of physico-chemical analyses. The existence of α-tetragonal, β-monoclinic solid solutions on the basis of the initial compounds and the intermediate γ-phase, which crystallizes in Fdd2 space group, has been established. The γ-phase forms the eutectics with the initial components. Their coordinates are: 42 mol.% GeS_2 (1121 K) and 93 mol.% GeS_2 (1095 K).

Key words: phase diagram, solid solution, lattice parameters

The investigation of the $AgGaS_2$–GeS_2 section is a part of systematic studies of the quasiternary system Ag_2S–Ga_2S_3–GeS_2 and the reciprocal system $AgGaSe_2$ + $GeS_2 \Leftrightarrow AgGaS_2 + GeSe_2$. The compounds of $A^IB^{III}C_2^{VI}$ type are perspective materials for quantum electronics [1–4]. The study of the solubility of the $D^{IV}C_2^{VI}$ compounds in $A^IB^{III}C_2^{VI}$ draws attention to it for the purpose of increasing of two-ray s-refraction and the increasing of transparency region [5,6].

The data concerning the investigation of the phase equilibria in the $AgGaS_2$–GeS_2 system can be found in [7], Fig. 1.

Discrepancies caused the necessity to study of the system in the full concentration range again. The purpose of this work was the establishment of the homogeneity ranges of the phases in order to obtain new nonlinear optical materials.

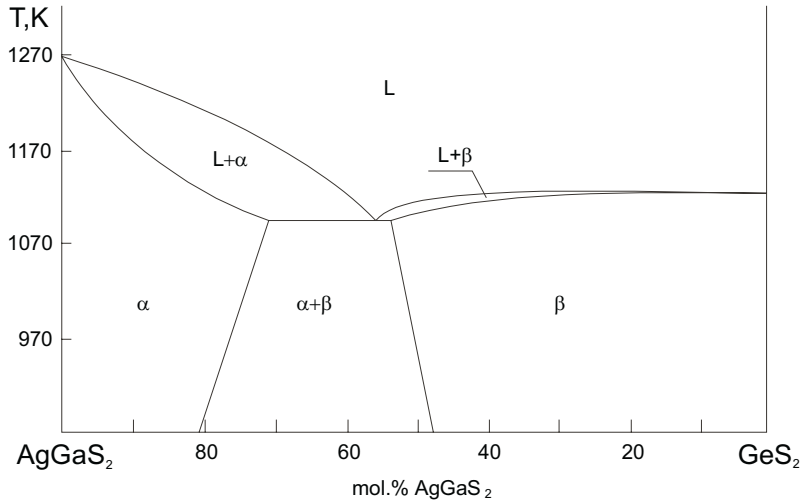

Figure 1. Phase diagram of the quasi-binary section $AgGaS_2$–GeS_2 [7].

$AgGaS_2$ crystallizes in space group $I\bar{4}2d$, with the lattice parameters $a = 0.05755$, $c = 1.0298$ nm, which agrees well with [8]. The temperature of the congruent melting is 1271 K. Germanium disulfide melts congruently at 1121 K. According to [9], the diffractogram of the compound has been indexed in monoclinic system, space group $P2_1/c$ with the lattice parameters $a = 0.6751$, $b = 1.6796$, $c = 1.1436$ nm, $\beta = 90.8568$.

EXPERIMENTAL

The alloys synthesis, belonging to the $AgGaS_2$–GeS_2 section, was carried out from the elementary components (Ag – 99.997%, Ga – 99.997%, Ge – 99.9999 %) in evacuated to 0.1 Pa quartz ampoules with vibrational mixing. The highest temperature was 1370 K. Alloys on the basis of $AgGaS_2$ increase their volume during cooling [8], and double containers were used to avoid oxidation. Homogenization of the obtained alloys took place at 720 K during 1000 hours. Further they were quenched in cool water. Samples obtained in this way have been investigated using the methods of differential thermal analysis (DTA), and X-ray phase and microstructural (MSA) analyses. DTA was carried out using VDTA-8M3 thermograph, which was calibrated against the melting points of different metals. Tungsten powder was chosen as a standard. The samples investigated were heated with the rate 5 K/min. Temperature was controlled by thermocouple W–Re0.05/W–Re0.2. X-ray phase analysis was performed using DRON–4–13 diffractometer (CuK_α radiation).

For the definition of the reflection intensities and angles, the shooting took place in step mode, scanning step $2\Theta = 0.02°$ with the exposition time in every point 10 seconds. Results of X-ray analysis have been worked up by the PD Win program complex. MSA has been carried out using microscope MMU–3.

RESULTS AND DISCUSSION

DTA results are presented in Table 1. As one can see, the initial compounds $AgGaS_2$ and GeS_2 melt congruently at 1271 K and 1121 K, respectively, which agrees well with literature. The character of solidus curves changes in the ranges of 0–30 mol.% GeS_2 and 98–100 mol.% GeS_2 testifies the crystallization of the solid solutions on the basis of the initial compounds. Results of X-ray analysis are presented in Fig. 2. The solid solution on the basis of $AgGaS_2$ extends to about 30 mol.% GeS_2. The lattice parameters change from $a = 0.57559(1)$, $c = 1.02998(3)$ nm for $AgGaS_2$ to $a = 0.57166(3)$, $c = 0.99695(6)$ nm for limiting composition of the solid solution.

Table 1. DTA results of the alloys of the quasi-binary section $AgGaS_2$–GeS_2.

No	Phase composition, mol.%		Temperature of thermal effects on the DTA, K	
	$AgGaS_2$	GeS_2	T – liquidus	T – solidus
1	100	–	1271	–
2	95	5	1267	1250
3	90	10	1253	1225
4	85	15	1238	1198

Table 1 (continuation)

5	80	20	1225	1173
6	75	25	1203	1152
7	70	30	1185	1130
8	65	35	1165	1121
9	60	40	1137	1121
10	55	45	1128	1121
11	52	48	1130	1120
12	50	50	1133	1125
13	48	52	1136	–
14	45	55	1135	1125
15	42	58	1134	1045
16	40	60	1133	1095
17	35	65	1129	1096
18	30	70	1128	1103
19	25	75	1125	1097
20	20	80	1119	1092
21	15	85	1113	1094
22	12	88	1109	1095
23	10	90	1106	1088
24	8	92	1102	1095
25	5	95	1105	1093
26	2	98	1112	–
27	–	100	1121	

The extent of the solid solutions on the basis of GeS_2 does not exceed 2 mol.% $AgGaS_2$. They crystallize in the monoclinic system, space group $P2_1/c$. In the concentration range of 48–55 mol.% GeS_2 (for T = 720 K) the γ-phase of variable composition ($Ag_xGa_xGe_{1-x}S_2$) exists. The diffractogram of the alloy with composition $AgGaGeS_4$ indexes in rhombic system, space group *Fdd*2 [10] with the lattice parameters a = 1.20152(2), b = 2.2904(1), c = 0.68742(4) nm. Within the homogeneity range of the γ-phase the lattice parameters change from a = 1.2028(3), b = 2.2950(1), c = 0.6879(1) for x = 0.52 to a = 1.20023(3), b = 2.28817(7), c = 0.68730(2) for the composition with x = 0.45. Results of MSA are in good agreement with the results obtained by the X-ray analysis.

On the basis of the obtained results the phase diagram of the $AgGaS_2$–GeS_2 system have been constructed (Fig. 3). Liquidus of the system contains three branches of primary phase crystallization: α-solid solutions on the basis of $AgGaS_2$ (0–42 mol.% GeS_2), intermediate γ-phase (42–93 mol.% GeS_2) and β-solid solutions on the basis of GeS_2 (93–100 mol.% GeS_2). The intermediate rhombic phase forms the eutectics with the initial components. Their coordinates are: e_1 – 42 mol.% GeS_2, 1121 K and e_2

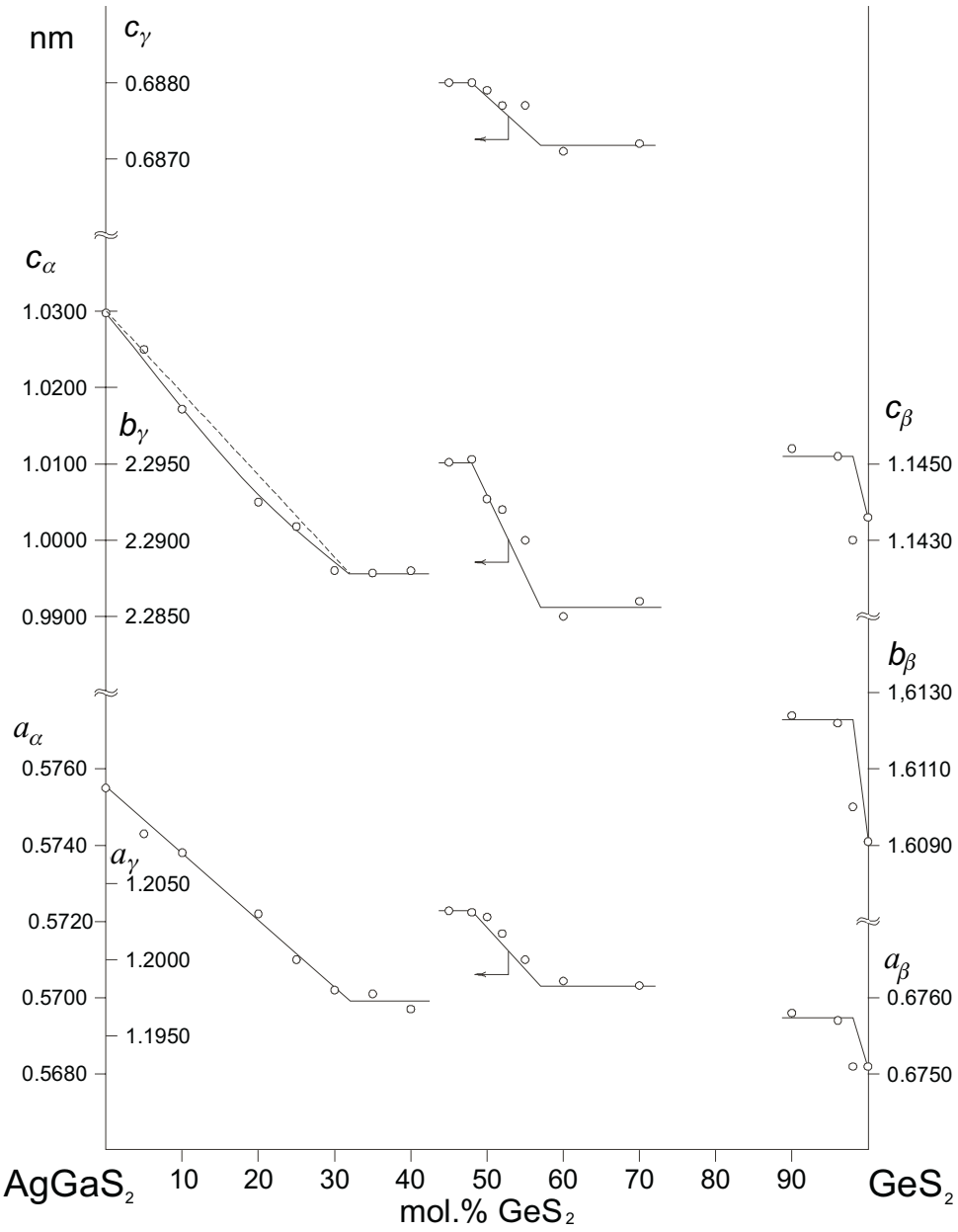

Figure 2. Plots of lattice parameters and unit cell volumes of the solid solutions in the quasi-binary section $AgGaS_2$–GeS_2 (at 720 K).

– 93 mol.% GeS_2, 1095 K. So, the investigations that have been carried out, showed that the phase diagram which was constructed in [7], differs essentially from that in the present work. One can assume, that in [7] the alloys were not equilibrated before the physico-chemical investigations, leading to a false phase diagram.

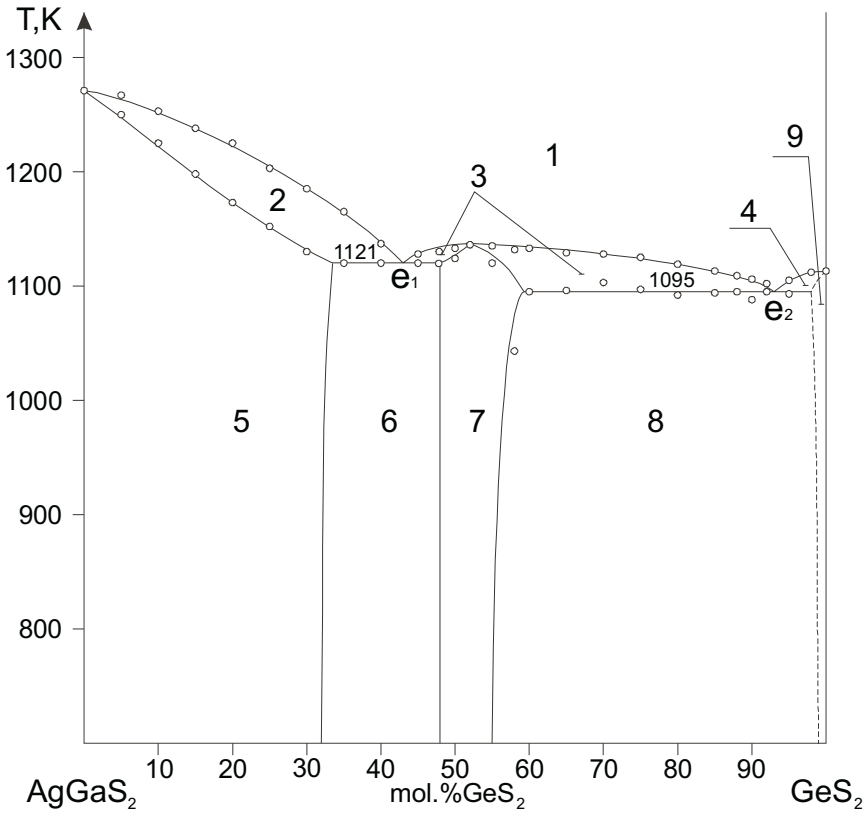

Figure 3. Phase diagram of the quasi-binary section $AgGaS_2$–GeS_2: 1 – L, 2 – L + α, 3 – L + γ, 4 – L + β, 5 – α, 6 – α + γ, 7 – γ, 8 – γ + β, 9 – β.

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